A NEW PERFORMANCE TEST TO ASSESS THE POTENTIAL DELETERIOUS EFFECT OF SULPHIDE-BEARING AGGREGATES FOR CONCRETE

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ABSTRACT

Recently, important damages in concrete containing sulfide-bearing aggregates were observed in the Trois-Rivières area (Québec, Canada). More than 1000 residential owners and many commercial buildings have faced serious issues related to the deterioration of their concrete housing foundations and slabs. The problematic aggregate is an anorthositic gabbro containing sulfide minerals. These sulfide minerals are unstable in the presence of oxygen and humidity resulting in an oxidation reaction; and pyrrhotite is known as one of the most "reactive" sulfide minerals.

The goal of this research is to develop a performance test to assess the potential deleterious effect of different sulfide-bearing aggregates for concrete. So far, the chemical approach, using a measure of the total sulfur content is a tool used for the rapid detection of the presence of iron sulfides in aggregate. This technique cannot identify the type of sulfide present and serves only as a screening test and further testing is needed. In the approach proposed, the next step is a newly-developed mortar bar expansion test where the bars are subjected to a cyclic exposure conditioning regime involving wetting and drying cycles in an oxidizing agent keeping temperature and humidity conditions that are favorable to oxidation reaction.

1 INTRODUCTION

Cases of rapid degradation of concrete associated to iron sulfides in aggregates were recently recognized in the Trois-Rivières area. More than 1000 residential and commercial owners have faced serious issues related to the deterioration of their concrete foundations and slabs. In some cases, the deterioration was such that immediate remedial actions were required and concrete has to be replaced (figure 1). All the masonry and covering stones were first removed because they stand on the foundation walls and permit to lighten the structure. Houses were lifted up from their foundations and the later was demolished and replaced.

The signs of concrete deterioration observed in the distressed concretes mainly consist of map cracking on the surface of the walls with some crack openings reaching more than 40mm. Yellowish and brownish discoloration was often observed surrounding these cracks. Pop-outs are observed on the walls showing the presence of oxidized and rusted aggregate particles. Small bumps easily detachable from below showing oxidized and rusted aggregate particles can be seen. Some of these deterioration features are illustrated in figure 2.

Figure 1: Replacement of the concrete foundation. All the masonry and covering stones were removed, houses were lifted up and concrete foundations were demolished and replaced.

A large number of concrete samples were investigated. In all cases, the aggregate material used for the concrete manufacturing was an intrusive igneous rock, more precisely an anorthositic gabbro, containing various proportions of sulfide minerals including pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$), chalcopyrite ($CuFeS_2$) and pentlandite ($(Fe,Ni)_9S_8$). Figure 3 presents views of the anorthositic gabbro particles on fresh and polished surfaces.

Iron sulfides are common minor constituents in many rock types. Pyrrhotite, a non-stoichiometric mineral of general formula $Fe_{1-x}S$, with x varying from 0 (FeS) to 0.125 (Fe_7S_8) [1-2] is well known as an unstable mineral in the presence of oxygen and humidity. Belzile et al. 2004 [2] presented a review of pyrrhotite oxidation processes. A deleterious process involving the oxidation of sulfide minerals and the sulfatation of the cement paste is thought to have caused the swelling and cracking of the affected concrete elements. In fact, the presence of secondary reaction products including iron oxyhydroxide, gypsum, ettringite, ettringite/thaumasite solid solution and thaumasite was observed and support this hypothesis. The chemical reactions that lead to the oxidation of iron sulfide minerals and in turn the sulfate attack of the concrete are described in detail elsewhere [3,4].

Several publications have already identified the risks of sulfide oxidation for engineering works [5] but no precise guideline is available for the quality control of the aggregate materials. Until now, no study has been able to reproduce in the laboratory the expansion and deterioration of concrete containing sulfide bearing aggregates.

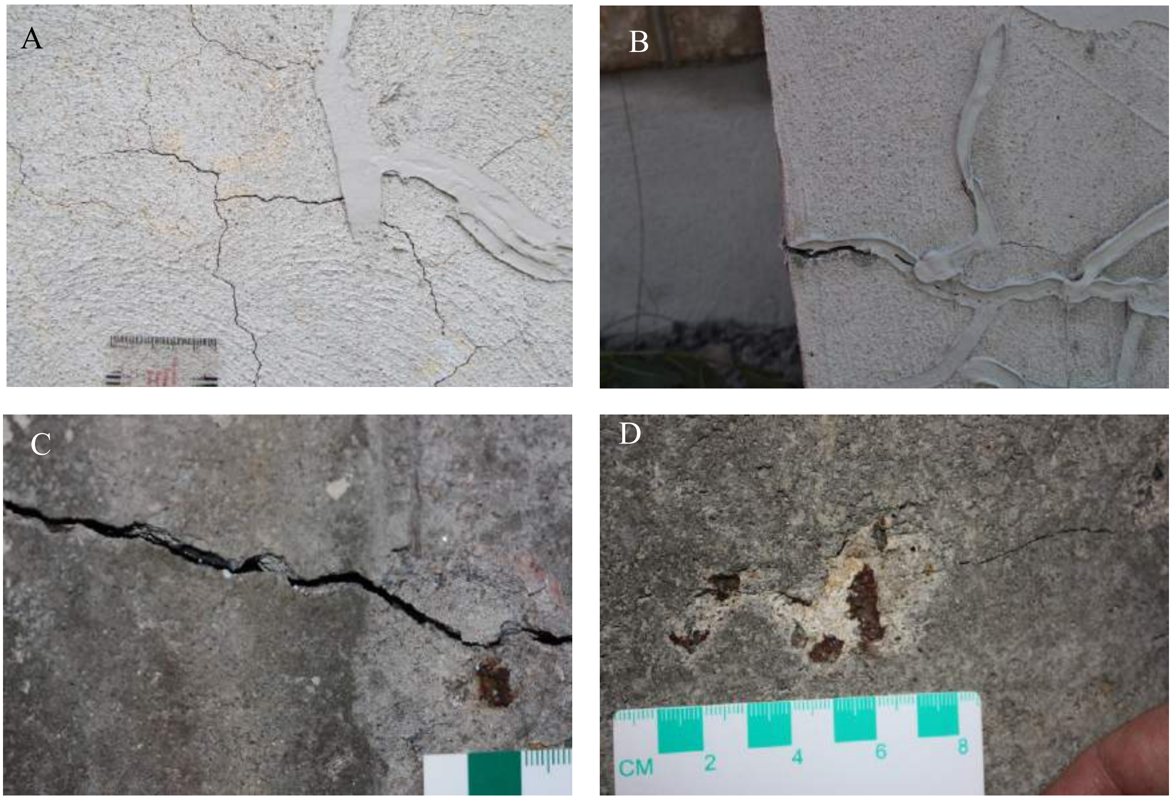

Figure 2: Examples of concrete deterioration features A – Map-cracking in concrete foundation showing some yellowish surface coloration. B – Cracks were filled up with sealant materials to prevent water infiltration. C – Large open cracks seen on the interior side close to an exposed oxidized aggregate particle. D – Pop outs on the interior side of a wall showing oxidized aggregates particles surrounded by whitish secondary products.

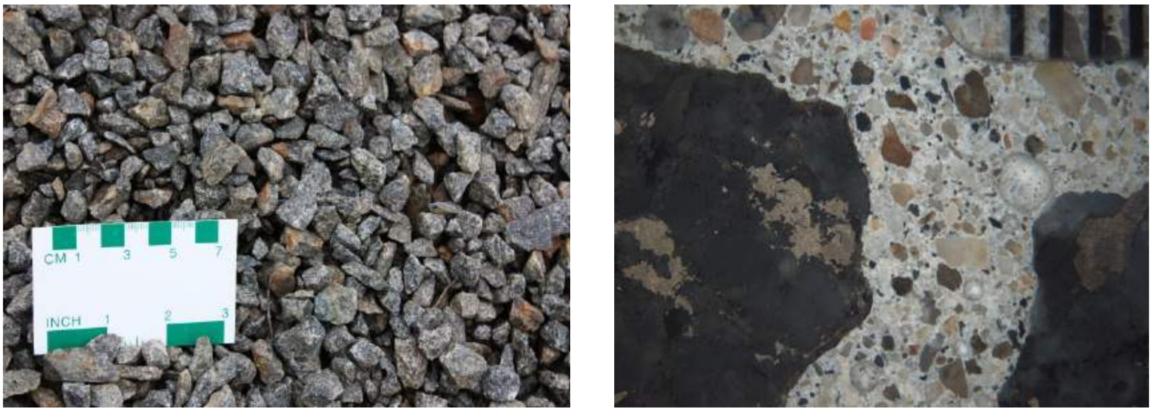

Figure 3: Crushed anorthositic gabbro coarse aggregate particles with a stereomicroscopic view of a polished sample showing aggregate particles containing iron sulfide minerals.

2 MATERIALS AND METHODS

The main material used in this study is the anorthositic gabbro (problematic aggregate) from the Saint-Boniface quarries, in the Trois-Rivières area, Québec, Canada. Aggregate materials without sulfide minerals are used as control specimen. A total of 8 aggregates were studied including 6 sulfide-bearing aggregates and 2 control aggregates.

The chemical approach, using a measurement of the total sulfur content is a tool used for the rapid detection of the presence of sulfide minerals. Aggregate total sulfur content is used to get an approximation of the sulfide content calculated from mineral stoichiometry. This technique cannot identify the type of sulfide present and serves only as a screening test. The total sulfur content of aggregate material is determined by an infrared absorption method using an Eltra CS 800 carbon/sulfur analyzer. The sub-sample required for analysis is less than 1 g. A sample preparation method is proposed to avoid sampling bias.

Finally, a newly-developed mortar bar expansion test where the bars are subjected to a cyclic exposure conditioning regime involving wetting and drying cycles in an oxidizing agent keeping temperature and humidity conditions that are favorable to oxidation reaction is proposed. The goal of this test is to establish favorable conditions that will reproduce, in the laboratory, the expansive process responsible for the damage.

3 RESULTS AND DISCUSSION

3.1 Global evaluation program of concrete aggregate: 1st - Total sulfur content

Until now, the chemical approach, via a measurement of the total sulfur content, is a tool used for the rapid detection of the presence of iron sulfide minerals in an aggregate sample. In fact, the iron sulfide minerals are formed chemically by the presence of iron and sulfur. The measurement of the total sulfur content is used to calculate the sulfide content using iron sulfide minerals stoichiometry. For example, pyrite (FeS_2) contains 53.45% of S and pyrrhotite ($Fe_{1-x}S$) contains 37.67 % S. To determine the content of iron sulfide minerals, some assumptions must be made. First, almost all sulfide minerals contain sulfur, whether it is pyrrhotite, pyrite, chalcopyrite, ... so you cannot redistribute sulfur in different minerals unless data on the mineralogical distribution is known. The calculation is made from the stoichiometry of the minerals and does not consider substitutions or impurities.

The total sulfur content is often determined by an infrared absorption method with a carbon/sulfur analyzer. This device consists of sample combustion in an induction furnace and measurement of combustion gas absorption in the infrared region. For analysis, a sample of powder under 0.3 to 1 g is required. The sulfur content is measured from the SO_2 in the flue gas. Since the sub-sample required is less than 1 g, it is important that it is representative of the initial sample. Sampling bias and preferential grinding of soft phases may be avoided.

Following critical evaluation of sample preparation methods suggested in the CAN/CSA-A23.2-26A-09 (Determination of Potential Alkali-Carbonate Reactivity of Quarried Carbonate Rocks by Chemical Composition) and in the BNQ 2560-500/2003 (Aggregates - Determination of the petrographic index of the potential sulfate swelling for granular materials), a sample preparation method was developed and used for all aggregate samples analyzed in this study (Figure 4).

An initial sample of 4 kg, with particle size ranging between 5 and 20 mm, is split in two representative subsamples containing more than 300 particles each. A portion of 2 kg is then crushed to reduce all particles to a size less than 5 mm. The sample is split until a sub-sample of 500 g is obtained (2 splits). The sub-sample of 500 g is then pulverized so that all particles are less than 300 microns. The sample is then split until a mass of 50 g is obtained (3 splits). The sample, with a weight of about 50 g, is entirely pulverized until all particles are less than 80 microns in size. The resulting sample is split in 4 parts for the different chemical analyzes.

To validate the assay variability on the total sulfur content measurement, samples of different types of aggregate materials were prepared and split into four portions to be analyzed in four different laboratories. For quality controls, some blanks and duplicates were also analyzed. Similarly, standard samples were included in each series of analysis. Table 1 presents the results obtained by each laboratory as well as key statistics, mean, standard deviation and coefficient of variation.

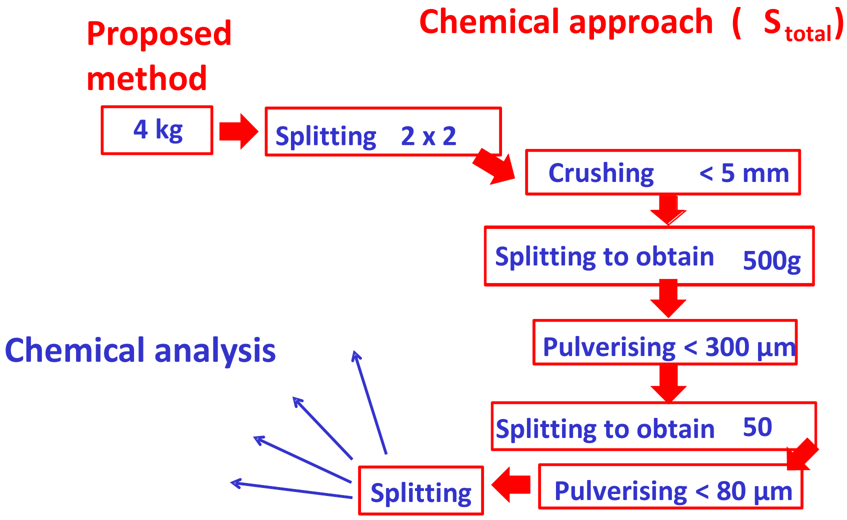

Figure 4: Sample preparation method to ensure that the sub-samples obtained are the most representative as possible as the initial sample.

The results obtained show that the inter-laboratory variability is acceptable, with values of the coefficient of variation lower than 10% for most of the samples analyzed. Higher coefficient of variation values correspond to samples with very low total sulfur content in order of 0.1% or less. Duplicates samples (5 and 5-bis and 10 and 10-bis) show little variation and present the same mean values. Similarly, the values obtained for the standard sample, CVT-1 corresponds to the published values. We can conclude that the results are accurate and precise and can be used as a screening tool in the global evaluation program.

3.2 Global evaluation program of concrete aggregate: 3rd - Mortar bar expansion test

The oxidation of iron sulfide minerals generates secondary reaction products such as iron oxyhydroxides (goethite , limonite , ...) products. This reaction generates also sulfuric acid that reacts with the cement paste components producing internal sulfate attack with presence of gypsum, ettringite and thaumasite. All these secondary minerals have a higher volume than the reactants and are responsible for the swelling and cracking of the concrete.

The objective of this section is to develop a performance test on mortar bars to reproduce in the laboratory the expansion observed on the affected concrete caused firstly by the oxidation of the sulfide-bearing aggregate followed by the sulfate attack of the cement paste.

Table 1. Results of the total sulfur content measured by 4 laboratories

Sample	Lab 1 S (%)	Lab 2 S (%)	Lab 3 S (%)	Lab 4 S (%)	Mean	σ	CV (%)
1	0.44	0.44	0.4	0.38	0.42	0.03	7.2
2	1.71	1.72	1.54	1.68	1.66	0.083	5
3	0.59	0.57	0.48	0.46	0.53	0.065	12.3
4	1.68	1.74	1.63	1.64	1.67	0.05	3
5	0.05	0.03	<0.02	0.03	0.04	0.012	31.5
5 - bis	0.05	0.03	0.03		0.04	0.012	31.5
6	0.04	0.03	0.02	0.01	0.03	0.025	51.6
7	0.03	0.02	<0.02	0.01	0.02	0.01	50
8	0.81	0.76	0.74	0.75	0.77	0.031	4.1
9	0.88	0.83	0.84	0.84	0.85	0.022	2.6
10	0.12	0.1	0.09	0.09	0.10	0.014	14.1
10 - bis	0.12	0.08	0.09		0.10	0.021	21.5
11*	0.01	<0.005	<0.02	0.01	0.01	0	0
12	1.43	1.32	1.43	1.42	1.40	0.054	3.8
13	0.01	0.01	<0.02		0.01	0	0
14	0.02	0.02	<0.02		0.02	0	0
15	0.003	0.002	<0.02		0.003	0.001	28.3
16	0.004	0.005	<0.02		0.005	0.001	15.7
17	0.05	0.04	0.04		0.04	0.006	13.3
18	0.05	0.04	0.04		0.04	0.006	13.3
19	0.06	0.05	0.05		0.05	0.006	10.8
20	0.06	0.05	0.06		0.06	0.006	10.2
21	0.1	0.09	0.1		0.10	0.006	6
22	0.11	0.09	0.1		0.10	0.01	10
23	0.15	0.16	0.16		0.16	0.006	3.7
24	0.25	0.23	0.26		0.25	0.015	6.2
25	0.23	0.24	0.26		0.24	0.015	6.3
26	0.31	0.29	0.3		0.30	0.01	3.3
27	0.34	0.33	0.34		0.34	0.006	1.7
28	0.35	0.37	0.4		0.37	0.025	6.7
29	0.38	0.4	0.44		0.41	0.031	7.5
30	0.45	0.49	0.54		0.49	0.045	9.1
CVT-1*	0.25	0.26	0.25		0.25	0.007	2.8

*11 is a blank *CVT-1 is a standard with published value = 0.26 σ 0.05 (n = 5-37)

Preliminary tests were carried out on mortar bars specimens in different conditions of humidity, temperature and using different oxidizing solutions in order to establish favorable conditions for the development of a performance test that will reproduce, in the laboratory, the expansive process responsible for the damage of the concrete incorporating sulfide-bearing aggregates. Mortar bars, 25x25x28.5 mm in size, were manufactured using a water-to-cement ratio (w/c) of 0.70 and a cement-to-aggregate ratio of 1:2.72. A high w/c was chosen to reproduce the characteristics of concrete used in the damaged housing foundations.

The grading requirement for aggregate used was the same as that used in the standard test method for potential alkali reactivity of aggregates (mortar bar method) (CAN/CSA A23.2-25A). All the bars were prepared with a general use (GU) portland cement. A total of 8 types of aggregates with different sulfides contents, including 2 control specimens without sulfide minerals, were used in this experiment. In order to reproduce the deterioration observed in the field, the test was divided in two phases: the first promotes conditions favorable for the oxidation of the aggregate and the second promotes the sulfate attack of the cement paste.

According to [2], the oxidation reaction of pyrrhotite is enhanced at high temperature and humidity. To promote the oxidation of sulfides, mortar bars were stored at different temperatures (21°C, 38°C, 60°C and 80°C), at three different relative humidity (60, 80 and 100%) with wetting and drying cycles in oxidizing solutions. The mortar bars were soaked twice per week for a 3-hour period into a 6% sodium hypochlorite solution (bleach) or a 3% hydrogen peroxide solution, and then replaced under their respective controlled temperature and humidity conditions. Mass and length measurements were monitored once a week. After 3 months in these conditions favorable to the oxidation reaction, the mortar bars were transferred to 4°C and 100% relative humidity to promote the sulfate attack.

Figure 5 presents the influence of the temperature on the expansion obtained with the Maskimo aggregate. All mortar bars were kept at 80% relative humidity with 2 wetting and drying cycles per week in the sodium hypochlorite solution. A temperature of 80°C increases the expansion due to the oxidation of the sulfide bearing aggregate. Figure 6 presents the expansion obtained for the mortar bars kept at 80°C and 80% relative humidity with 2 wetting cycles per week in the sodium hypochlorite solution. A set of bar was transferred at 4°C after 90 days; these conditions increased the rate of expansion. Photographs of the samples after the expansion test are also presented. Maskimo samples present polygonal cracks that often originate from oxidized aggregate particles. Many aggregate particles are covered with rust. Control samples are intact despite the severe conditions they were exposed to.

Different parameters were tested in the mortar expansion test. Two oxidizing solutions (sodium hypochlorite (bleach) and hydrogen peroxide solutions) were used to soak the bars twice a week. However, expansion was obtained only with the sodium hypochlorite solution. Shrinkage of the mortar bars was obtained using the hydrogen peroxide due to its lower pH that promotes the neutralisation of the solution while in contact of the mortar bars. In the first part of the test (in the oxidation phase) different temperatures were tested (21, 38, 60 and 80°C) and it was clear that the higher the temperature was, the greater was the expansion measured. Samples were stored at 60, 80 and 100% relative humidity. Both 60 and 80% relative humidity gave similar results. Finally, higher expansion is obtained if the mortar bars are transferred at 4°C after 3 months at high temperature to promote the sulfate attack.

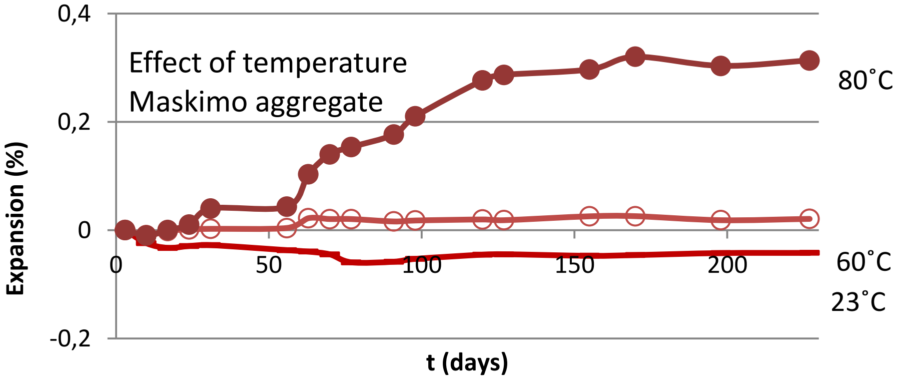

Figure 5: Expansion of mortar bars as a function of time for samples with Maskimo aggregate stored at different temperatures.

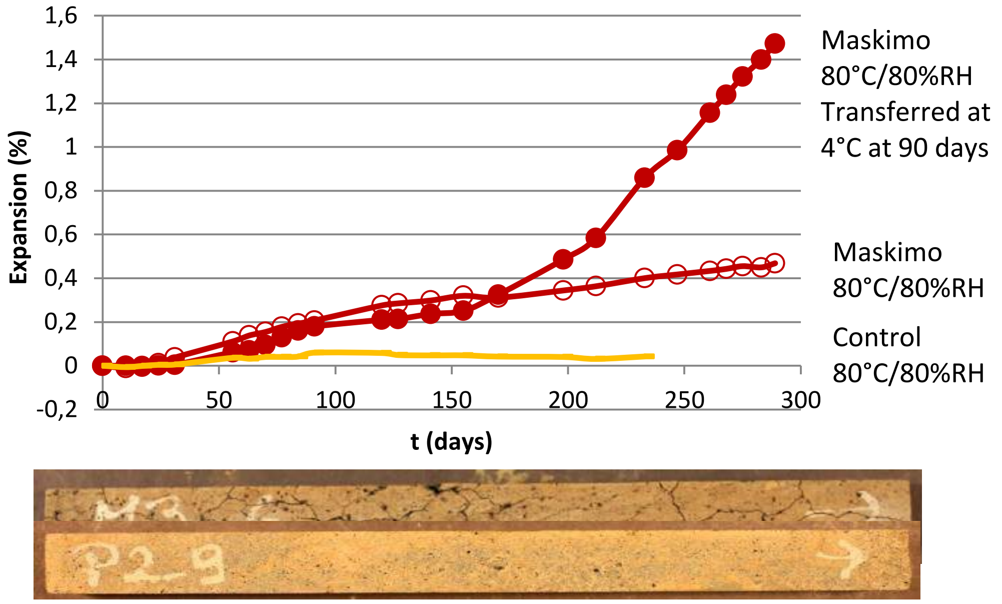

Figure 6: Effect of the storage conditions on the expansion reached by the of mortar bars with Maskimo aggregate. Control sample was kept in the same conditions. Examples of mortar bars at the end of the experiment: Maskimo aggregate (top) and control (bottom).

4 CONCLUSIONS

The goal of this study was to develop a global evaluation program of concrete aggregate to identify potentially deleterious sulfide-bearing aggregates prior to their use in concrete. The approach proposed begins by a measure of the total sulfide content of the aggregate. After, the aggregate was evaluated by a newly-developed mortar bar expansion test. Mortar bars were kept at 80°C and 80% relative humidity for 90 days with two 3-hour wetting and drying cycles a week in a 6% sodium hypochlorite solution. At 90 days, the bars were transferred at 4°C to promote the sulfate attack. The performance approach developed will be extended to a broader range of aggregates to establish the threshold values at each step of the protocol.

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